PB90-103805

Mechanisms of Nitrous Oxide Formation in Coal Flames

Energy and Environmental Research Corp., Irvine, CA

Prepared for:

Environmental Protection Agency, Research Triangle Park, NC

1989

U.S. Department of Commerce
National Technical Information Service
NTIS

AEERL-P-350

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completi

1. REPORT NO.	2.	3. PB90-103805
EPA/600/J-89/079		

4. TITLE AND SUBTITLE	5. REPORT DATE
Mechanisms of Nitrous Oxide Formation in Coal Flames	6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
J. C. Kramlich, J. A. Cole, J. M. McCarthy, W. S. Lanier (EERC); J. A. McSorley (EPA/AEERL)	

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Energy and Environmental Research Corporation 18 Mason Irvine, California 92718	11. CONTRACT/GRANT NO. 68-02-4247

12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
EPA, Office of Research and Development **Air and Energy Engineering Research Laboratory** **Research Triangle Park, NC 27711**	Journal Article; 8/87 14. SPONSORING AGENCY CODE **EPA/600/13**

15. SUPPLEMENTARY NOTES AEERL project officer is Joseph A. McSorley, Mail Drop 65, 919/541-2920. Combustion and Flame, 77:3 and 4, pp. 375-84 (9/89).

16. ABSTRACT The paper gives results of a study, using both detailed kinetic modeling and plug-flow simulator experiments, to investigate an unknown mechanism by which N2O is formed in coal flames. This mechanism has considerable importance in determining the influence of common and advanced NOx control strategies on N2O. Significant N2O emissions have been observed from coal and oil burning power plants but not from industrial gas flames, even when they are doped with an equivalent amount of fuel nitrogen. Kinetic modeling suggests that net N2O is unlikely to form within flame zones because of its rapid removal by: N2O + H yields N2 + OH. Also, reduction of NO on coal char, or coal char oxidation, can be significant N2O sources only if the rates are many times their published values. However, both kinetic modeling and experiments show that, if HCN appears in the gas phase between 1150 and 1500 K, it will be partially converted to N2O. The source of HCN may be either direct devolatilization or a char gasification reaction. This suggests that the N2O which appears in coal flames may originate from the homogeneous reaction of devolatilized char nitrogen in the fuel-lean post-flame region. The kinetics indicate that the formation is principally through the reaction: NCO + NO yields N2O + CO.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution Simulation	Pollution Control	13B 14G
Nitrogen Oxide (N2O)	Stationary Sources	07B
Flames		21B
Coal		21D
Kinetics		20K
Mathematical Models		12A

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Release to Public	**Unclassified**	11
	20. SECURITY CLASS *(This page)* **Unclassified**	22. PRICE

EPA Form 2220-1 (9-73)

EPA/600/J-89/079

COMBUSTION AND FLAME 77: 375–384 (1989)

Mechanisms of Nitrous Oxide Formation in Coal Flames

John C. Kramlich*, Jerald A. Cole, James M. McCarthy, and Wm. Steven Lanier

Energy and Environmental Research Corporation, Irvine, CA 92718

and

Joseph A. McSorley

Air and Energy Engineering Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Significant nitrous oxide (N_2O) emissions have been observed from coal and oil burning power plants, but not from industrial gas flames, even when they are doped with an equivalent amount of fuel nitrogen. The unknown mechanism by which this N_2O forms has considerable importance in determining the influence of common and advanced nitrogen oxide (NO_x) control strategies on N_2O. The present study uses both detailed kinetic modeling and plug-flow simulator experiments to investigate this mechanism. Kinetic modeling suggests that net N_2O is unlikely to form within flame zones because of its rapid removal by

$$N_2O + H \rightarrow N_2 + OH.$$

Also, reduction of nitric oxide (NO) on coal char can be a significant N_2O source only if the rates are many times their published values. However, both kinetic modeling and experiments show that if HCN appears in the gas phase between 1150 and 1500 K it will be partially converted to N_2O. The source of HCN may be either direct devolatilization, or a char gasification reaction. This suggests that the N_2O that appears in coal flames may originate from the homogeneous reaction of devolatilized char nitrogen in the fuel-lean postflame region. The kinetics indicate that the formation is principally through the reaction

$$NCO + NO \rightarrow N_2O + CO.$$

INTRODUCTION

The emission of nitrous oxide (N_2O) from stationary combustion sources has received relatively little attention compared to that given to other fixed nitrogen forms. This is in spite of the fact that it is an environmental pollutant of some consequence. For example, transport of N_2O across the tropopause is a major source of stratospheric nitric oxide (NO) [1, 2]. This occurs when the reaction of N_2O with singlet oxygen produces NO, which enters into the ozone destruction chemistry cycle [3]. Nitrous oxide is also an efficient absorber of infrared radiation and thus is a potential "greenhouse-effect" gas [4–6].

The existence of an important anthropogenic source flux has been well established. The principal evidence is the observed 0.2%–0.3% annual increase for tropospheric N_2O [7]. Uncertainties in the source, sink, and accumulation terms have, however, prevented firm identification of the importance of the various sources. A recent study by Hao et al. [8] suggests that global N_2O sources exceed the sinks by about 30%, and that most of

* Corresponding author.

Published by Elsevier Science Publishing Co., Inc.
655 Avenue of the Americas, New York, NY 10010

0010-2180/89/$00.00

NTIS is authorized to reproduce and sell this report. Permission for further reproduction must be obtained from the copyright owner.

this excess can be attributed to fossil fuel combustion. If so, this implies that fossil fuel combustion represents an important source flux; however, this conclusion cannot be considered as highly certain due to reasons discussed below.

Nitrous oxide emissions from electric utility power plants have been measured by a number of investigators [8–11]. The emissions from gas-fired flames were never greater than 11 ppm, and were frequently much less. Sub-scale tunnel furnace experiments in which a propane flame was doped with ammonia (NH_3) (N = 1% of fuel by weight) yielded very high nitrogen oxide (NO_x) values, but less than 5 ppm N_2O [12]. (During the present study, work with the improved analytical techniques described below showed the N_2O emissions from these experiments were less than 1 ppm.) The conclusion is that industrial gas flames are not strong emitters of N_2O, even when large amounts of fuel-nitrogen are present. Therefore, the high N_2O emissions found from the coal and oil flames described in the following paragraphs must be due to some special attribute that is unique to these flames.

Field measurements of coal and oil fired power plants show a wide variation of N_2O emissions, from 10 to 208 ppm [8–11]. Some data have suggested that N_2O molar emissions could be estimated as about 25% of the NO_x [10, 11]. Recent expansions in the database do not support this correlation, however [13].

The characterization of N_2O emissions has become more complex due to the recent discovery of a major sampling artifact [14]. Field sampling normally involves the filling of sample containers, with the subsequent analysis taking place at a remote laboratory. The results show that the NO is converted into N_2O within the container by a reaction whose overall time constant is of the order of 2 hours. Each mole of NO appears to convert into as much as 0.40 mol of N_2O, depending on conditions. The necessary reagents are NO, O_2, SO_2, and moisture at concentrations that are representative of coal combustion flue gas. The proposed mechanism involves the oxidation of NO to NO_2, followed by absorption into surface moisture or condensate, chemical reaction, and release as N_2O [15]. This implies that the artifact can dominate results from coal and oil flames, but not sulfur-free gas flames.

No satisfactory theory of N_2O formation in industrial flames has yet appeared. The development of such a theory is necessary to understand the influence of combustor type or NO_x control strategies on N_2O emissions. Also, knowledge of the mechanism may suggest simple combustion modifications for N_2O control.

This article describes results of detailed chemical kinetic calculations and experiments directed at defining the N_2O formation mechanism in coal flames. The kinetic modeling work was used, along with previous data, to focus the formulation and testing of hypotheses. The experimental effort was then directed to critical tests of the hypotheses.

NUMERICAL SIMULATION

Numerical Tools

The kinetics calculations were performed using a stirred reactor/plug-flow algorithm [16]. The key feature of this method is the use of a small stirred reactor as an ignition source for a plug-flow reactor. The program also has the capability of arbitrarily specifying time–temperature histories within the reactor, and the ability to introduce sidestream fluxes of reactants at arbitrary points within the plug-flow system. The model considers concurrent heterogeneous reactions by numerically treating these in quasi-homogeneous form. The calculations described in this article were performed using the kinetic reaction mechanism recently published by Glarborg et al. [17].

Homogeneous Chemistry

Industrial gas flames have not been observed to emit large amounts of N_2O, even when doped with fuel nitrogen. This observation suggests that either N_2O is not formed within the flame, or that the formation is balanced by a fast destruction step. This behavior was briefly examined using the homogeneous chemical model.

For this simulation the flame zone was ignited by a stirred reactor of 1.0 ms residence time

TABLE 1

Important Flame Reactions

NH_3 reaction:	
1.	$NH_3 + OH \rightarrow NH_2 + H_2O$
2.	$NH_2 + OH \rightarrow NH + H_2O$
3.	$NH + NO \rightarrow N_2O + H$
4.	$NH + O$ or $OH \rightarrow NO$, Eventually
HCN reactions	
5.	$HCN + OH \rightarrow HNCO + H$
6.	$HNCO + H \rightarrow NH_2 + CO$
7.	$HNCO + OH \rightarrow NCO + H_2O$
8.	$HCN + O \rightarrow NCO + H$
9.	$NCO + NO \rightarrow N_2O + CO$
10.	$NCO + OH \rightarrow NO + CO + H$
N_2O destruction	
11.	$N_2O + H \rightarrow N_2 + OH$

operating on methane and air (1700 K, fuel–air equivalence ratio or $\Phi_{FA} = 0.8$). The effluent fed into a plug flow reactor, which was quenched at 275 K/s. With both HCN and NH_3 doped into the flame zone (N = 1% of fuel by weight), final N_2O emissions were less than 0.01 ppm. In spite of these insignificant final emissions, the N_2O chemistry was found to be quite active within the flame zone.

Table 1 summarizes the most active nitrogen reactions in the flame zone. For NH_3 doping, Reactions 3 and 4 are in competition for the available NH pool. The high concentrations of O and OH in the flame zone favor Reaction 4, which reduces the NH concentration, and therefore reduces N_2O formation via Reaction 3. Any N_2O that is formed is quantitatively removed by Reaction 11.

The reactions for HCN doping are also shown in Table 1. The HCN reaction paths lead through either HNCO or NCO. The HNCO path leads to NH_2 via Reaction 6, and into the NH_3 chemistry just described, or it can lead to NCO through Reaction 7. The NCO intermediate can form N_2O in Reaction 9. Again, any N_2O formed in the flame is almost quantitatively removed by Reaction 11.

A reaction rate sensitivity analysis showed that Reaction 11 is fully capable of removing flame zone N_2O, even if the formation chemistry is unrealistically augmented. This concurs with strong experimental evidence that N_2O does not survive long into the postflame regions of laminar, premixed flames [18]. The fact that measurable N_2O is emitted from large-scale gas flames could be due to the turbulent quench of reacting packets before N_2O destruction is complete. However, the high rate of Reaction 11 suggests that the flame zone is not the source of N_2O in coal combustion.

Heterogeneous Chemistry

One means of avoiding fast reduction by Reaction 11 is for the N_2O formation to occur downstream of the flame zone, where Reaction 11 is slowed by lower temperatures and reduced hydrogen atom concentrations. In a coal flame the char may provide a vehicle for carrying fixed nitrogen beyond the volatile flame zone. Potential sources of N_2O include the following:

1. The oxidation of char nitrogen to N_2O.
2. The reaction of NO with char nitrogen, or the adsorption of an NO molecule onto the char surface where it subsequently reacts with a second NO molecule.
3. The devolatilization or gasification or char nitrogen, followed by gas-phase reaction.

The char oxidation option is mechanically very unlikely. The model was used to evaluate the feasibility of the other two options. A calculation format was adopted which modeled the tunnel furnace used for our earlier measurements [12]. This was configured as a 1.0-ms stirred reactor ignition zone followed by a 0.5-s fuel-rich stage and a 2.0-s fuel-lean stage ($\Phi_{FA} = 1.6$ and 0.8, respectively). The reaction starts at 1700 K and is quenched at a uniform rate of 275 K/s. The coal was assumed to devolatilize instantaneously to yield the composition shown in Table 2. The overall results were insensitive to reasonable variations in the chemical composition of the volatiles. The homogeneous chemistry was that used for the previous calculations [17]. The heterogeneous chemistry was limited to the four reactions shown in Table 3. In each case the rate has been left in the original units, although these were converted to internally consistent units for

TABLE 2

Coal Reacting Composition

Constituent	Mass Percent
Volatile matter	
C_2H_2	28.6
HCN	0.95
H_2O	2.30
Char	
Carbon	64.0
Nitrogen	1.17
Hydrogen	2.98

calculations. A char particle size of 40 μm was assumed. The consumption of the char was assumed to occur via reduction in number density rather than reduction in particle diameter.

Figure 1 illustrate the results of the various cases. Case 1 shows the results of assuming all of the NO-char reduction products are N_2O. The reduction is assumed to occur at the rate proposed by Levy et al [21], and it results in minimal N_2O production. In Case 2, a competitive char nitrogen devolatilization step is included using the rate of Song et al [20]. This calculation assumes the devolatilization product to be NH_3, and it results in slightly over 2 ppm N_2O emissions. Case 3 repeats this calculation with HCN as the volatile species, and the results predict almost 100 ppm N_2O emissions.

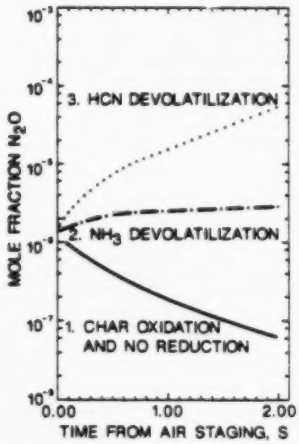

Fig. 1. Calculated N_2O histories for the fuel-lean zone of simulated staged coal combustion. All cases consider homogeneous chemistry. Case 1 considers concurrent char nitrogen oxidation and that NO reduction on char yields N_2O. Cases 2 and 3 also include NH_3 and HCN devolatilization, respectively.

TABLE 3

Heterogeneous Reactions

12.[a] $C(S) + O_2 \rightarrow CO_2$

$$d[C]/dt = -k_{12}A_E PO_2 \text{ (g/s)}$$
$$k_{12} = 204 \exp(-20{,}000/RT) \text{ gm/cm}^2\text{-atm-s}$$

13.[b] $N(S) + 1/2\ O_2 \rightarrow NO$

$$d[N]/dT = -k_{12}\,[N(S)/C(S)]A_E PO_2 \text{ gm/s}$$

14.[c] $NO + \text{char} \rightarrow 1/2\ N_2$

$$d[NO]/dt = k_{14}APO_2 \text{ mol/s-g}$$
$$k_{14} = 41{,}800 \exp(-34{,}700/RT) \text{ mol-g/m}^2\text{-atm-s}$$

15.[d] $N(S) \rightarrow HCN$

$$d[N]/dt = -k_{15}\,[N] \text{ g/s}$$
$$k_{15} = 5800 \exp(-29{,}100/RT) \text{ s}^{-1}$$

[a] Original rate [19] was for 0.1 atm O_2; this was generalized for assumed first-order O_2 dependence. Rate is per particle and A_E is the external area.

[b] Rate same as Reaction 12 based on the observed nonselectivity of N and C oxidation rates [20]. The instantaneous rate of N oxidation is the same as the C oxidation rate times the instantaneous N–C ratio.

[c] This rate [21] is normalized per gram of char. The external surface area, A, is in m^2/g.

[d] The rate of N volatilization [20] is reported as first order in char N.

These results suggest a plausible mechanism for N_2O formation in coal flames, which includes the following elements:

1. Char acts as a vehicle for conveying bound nitrogen away from the volatile flame zone.
2. A portion of this char-nitrogen devolatilizes as HCN within overall fuel-lean regions. Alternatively, HCN may be formed by gasification reactions [22].
3. A portion of the HCN reacts homogeneously to form N_2O via Reactions 8 and 9.
4. As this reaction occurs under postflame conditions, the reduced temperature and H-atom

concentrations prevent the removal of N_2O by Reaction 11.

These results also suggest that high N_2O concentrations can be formed without the presence of coal char if HCN is artificially introduced into a postflame environment at the proper temperature. This idea was tested by repeating the calculation performed under the "Homogeneous Chemistry" section above (i.e., Φ_{FA} = 0.8, 1.0-ms stirred reactor at 1700 K followed by a plug-flow reactor with a 275-K/s quench). The only difference was that the fixed nitrogen was introduced at various locations (i.e., temperatures) in the plug-flow reactor rather than in the flame zone. Note that this is a strictly homogeneous calculation.

Figure 2 shows that the introduction of HCN into the postflame region at temperatures between 1050 and 1400 K is predicted to result in a significant homogeneous N_2O formation. It also shows the results of a calculation in which Reaction 9 is assumed to branch 40% into N_2O + CO and 60% into N_2 + CO_2. This branching ratio, which has been observed as a lower limit at room temperature [23], substantially reduced predicted N_2O emissions. Ammonia does not convert nearly as efficiently to N_2O upon postflame injection.

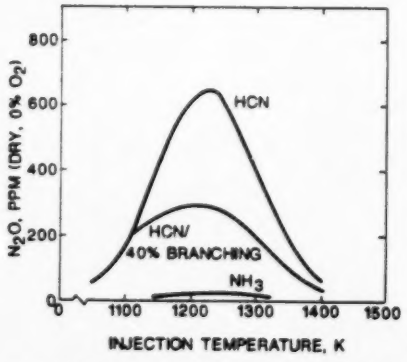

Fig. 2. Calculated N_2O emissions from a quenched plug-flow reactor into which NH_3 and HCN were introduced at various axial locations (temperatures). Conditions: fuel-lean natural gas combustion (Φ_{FA} = 0.8) with 600 ppm NO; HCN or NH_3 added to equivalent of 900 ppm averaged over the reactor.

An evaluation of the reaction kinetics showed that the behavior was due to the following:

1. At high temperature, the reaction rate of NCO oxidation (Reaction 10) competes favorably with N_2O formation. Also, the removal of N_2O via Reaction 11 is more favored.
2. Within the N_2O formation window, both Reactions 8 and 9 are active.
3. At temperatures below the window, Reactions 5 and 6 dominate HCN consumption, and the production of the NCO needed for N_2O formation becomes insignificant.

In summary, the kinetic calculations predict that the appearance of HCN in a fuel-lean postflame region can result in a large N_2O emission. The literature suggests that devolatilization or gasification of char nitrogen may act as a source for this HCN.

EXPERIMENTS

Apparatus and Procedures

The experimental portion of this study was performed in a 21-kW refractory-lined tunnel furnace whose design has been detailed elsewhere [24]. The furnace is a 15.2-cm-i.d. by 2.7-m-long tunnel that has been designed to act as a plug-flow simulator. The furnace can be fired on either natural gas or goal. For the present experiments the entire furnace was fired under excess air (Φ_{FA} = 0.80). Under this operating condition the thermal quench rate throughout the region of interest was 350 K/s. Nitrogen-containing compounds were doped into the flow at various locations and temperatures along the reactor body.

Samples were collected by cooled probes, and filtered into evacuated 125-mL Pyrex flasks. For coal flame samples, 1.0 mL of 10 M NaOH was added to each flask before sampling; this was shown to prevent N_2O formation within the flask [14]. These were analyzed on a Perkin-Elmer Sigma-2 gas chromatograph equipped with an electron capture detector. A small aliquot was withdrawn from the flask and passed through a sample dryer (Aquasorb; P_2O_5) and into a 0.6-mL sample loop. The contents of the loop were flushed

into a 95% Ar/5 percent CH_4 carrier gas flowing at 20 mL/min. A 3-mm by 15-cm Porapak-Q precolumn at 70°C was used in an inject/backflush mode to protect the detector from contaminants. The separation was performed with a Molecular Sieve 5A column (60/80 mesh; 3 mm by 91 cm at 250°C). The detector was operated at 350°C, and sufficient makeup carrier gas was added to provide a total flow of 60 mL/min. Standards for calibration were prepared by dilution of known quantities of N_2O in an 11-L tank. The sensitivity was sufficient to observe the background N_2O concentration in the atmosphere (*ca.* 300 ppb) during air blank runs.

Solids samples for elemental analysis were obtained with a water spray quench probe, and the NO_x measurements used an extractive probe and chemiluminescent analysis [23]. Collected solids were analyzed for C, H, N, and ash on a Perkin-Elmer 240B elemental analyzer.

Homogeneous Results

The first test series was designed to determine if N_2O would appear in the tunnel furnace exhaust if fixed nitrogen compounds were artificially introduced into the postflame region. The furnace was fired on natural gas that was doped with sufficient NH_3 to provide a fuel-lean postflame environment containing 600 ppm NO. (All concentrations reported in this article are on a dry basis, and have been corrected to 0.0% excess air.) Nitrogen-containing compounds were added at various points in the reactor, with the HCN and NH_3 diluted in N_2. Acetonitrile was sprayed into the reactor as a water solution. Each additive was at an equivalent level of 900 ppm relative to the total reactor flow.

Figure 3 shows that significant N_2O emissions were formed for both HCN and acetonitrile addition. For acetonitrile the maximum occurred at 1400–1450 K, while for HCN the peak emissions are noted at 1250–1300 K. This shift is probably due to the delay in introducing the acetonitrile into the gas-phase caused by the droplet evaporation time. Both additives generate N_2O only over an approximately 300 K range, which Figure 2 suggests can be explained purely in

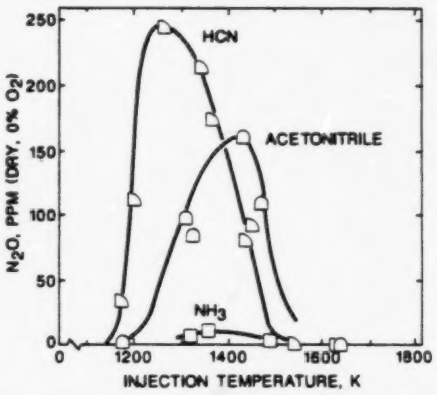

Fig. 3. Emissions of N_2O from the tunnel furnace for NH_3, HCN; and acetonitrile injection at various locations (temperatures). Conditions are identical to those of Fig. 2.

terms of chemical kinetics. The maximum yield of N_2O was approximately 245 ppm, which agrees much more closely with the Figure 2 predictions in which the NCO + NO reaction only branches 40% to N_2O. Note that NH_3 as an additive generates relatively minor amounts of N_2O, which agrees with the kinetic calculations shown in Fig. 2. These results demonstrate that the appearance of cyano species in the gas phase within specific temperature windows can result in N_2O emissions under realistic thermal environments. The key issue is whether (and how) cyano species may appear in the postflame region. Long-time nitrogen devolatilization and gasification have already been mentioned as candidates. Imperfect mixing in large-scale systems may also transport cyano species into cooler environments where N_2O formation is favored.

Coal Results

A limited number of results were obtained in an effort to relate coal flame behavior with N_2O formation. Figure 4 shows N_2O measurements at the exit of the tunnel furnace as a function of fuel-air equivalence ratio. The fuel is a high volatile B bituminous coal (Utah) with a 1.7% fuel-nitrogen constant. The results show that N_2O emissions are reduced under fuel-rich conditions. Under fuel-

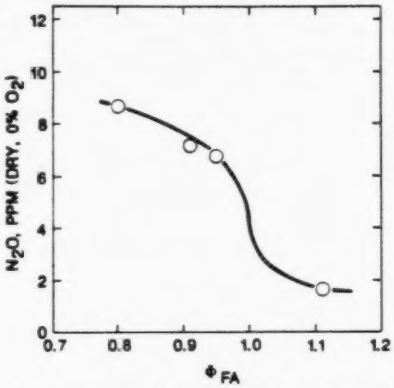

Fig. 4. Influence of stoichiometry on N_2O emissions from the tunnel furnace firing Utah high-volatile bituminous coal.

lean conditions the emissions are well in excess of the 1 ppm observed when an equivalent amount of fuel nitrogen is doped into a gas flame as NH_3 or HCN. These emissions correspond to an approximately 0.7% conversion of fuel-nitrogen into N_2O.

Char samples were extracted from the bituminous coal flame at $\Phi_{FA} = 0.8$ and analyzed for nitrogen and ash. Using ash content as a tracer, the char nitrogen at each point in the reactor could be expressed in equivalent ppm (i.e., that concentration resulting if the char nitrogen was quantitatively released from the char and mixed into the local gases without reaction). Figure 5 shows the measured car nitrogen, NO, and temperature profiles. The kinetics code was exercised over this condition as follows. A 1.0-ms residence time stirred reactor was used as an ignition source. Within this reactor the coal was assumed to devolatilize instantaneously to yield the composition shown in Table 2. In the subsequent plug-flow reactor the char nitrogen was added to the gas-phase reaction as a cross-stream flux along the length of the reactor. The rate at which the nitrogen was added is constrained to match the decay rate of char nitrogen noted in Fig. 5. The relative rates of Reactions 13 and 15 determined the composition of the added nitrogen, i.e., the NO/HCN ratio. The goal of the calculation was to examine time-resolved N_2O behavior through the kinetic model where the char-nitrogen contribution was defined experimentally. (The time-resolved behavior was examined through the model rather than experimentally due to the anticipated difficulty in obtaining unpurturbed samples from the flame zone with the present equipment. The literature suggests substantial in-probe reactions of N_2O when sampling from high-temperature reactive environments [18].)

The calculated N_2O profile in Fig. 5 shows several interesting features. First, note that the N_2O formation "window" defined by Fig. 3 (1150–1500 K) corresponds to residence times of 0.45–1.55 s. This means that a portion of the HCN released within that range of times will be emitted as N_2O. The N_2O transient that peaks at 0.35 s is the result of the high HCN flux into the gas phase in that region. However, the high N_2O removal rate due to Reaction 11 ensures that this N_2O does not contribute to the final emissions. Examination

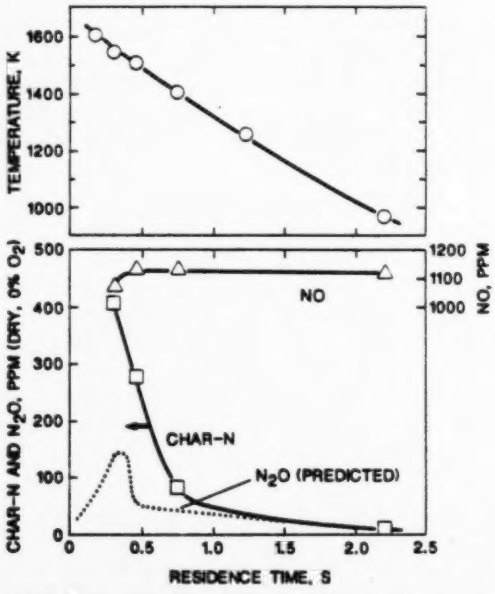

Fig. 5. Measured profiles of NO, char nitrogen, and temperature. The N_2O profile is calculated from the kinetic model using the char nitrogen decay rate to set the introduction rate of HCN and NO into the gas phase. The HCN–NO ratio is set from the expressions in Table 3.

of the char nitrogen loss kinetics shows that the total amount of char nitrogen lost as HCN after 0.45 s is only the equivalent of 16 ppm. This could then be viewed as the only reagent available for forming N_2O emissions. The calculated final N_2O emission value of 10 ppm compares well with the observed value of 8 ppm. This suggests that the low N_2O emissions in the coal-fired experiment are due to the fact that the bulk of the nitrogen is devolatilized into a gas stream that is too hot to support permanent N_2O formation. This is in comparison with Fig. 3 in which ample HCN was artificially introduced into the optimum region for N_2O formation, and high N_2O emissions resulted.

One motivation for conducting this work is to understand the influence that NO_x control strategies have on N_2O emissions. Fuel staging, or reburning, is an NO_x control approach designed principally for large boilers in which a portion of the fuel is injected after the main flame zone. This drives the overall stoichiometry to a fuel-rich value. After a certain time in the fuel-rich zone, air is added to fully burn out any remaining fuel. This lean/rich/lean sequence can result in significant NO_x reduction.

The influence of two aspects of reburning on N_2O emission was briefly examined. In the first, Utah coal was applied in the tunnel furnace as a reburning fuel to a natural-gas-fired primary stage. The primary, secondary, and burnout zone equivalence ratios were 0.9, 1.1, and 0.8, respectively. Figure 6 shows a significant increase in N_2O emissions relative to the baseline. For these results, the efficiency of conversion of coal nitrogen to N_2O is approximately 6.5%. The results of Fig. 4 show a 0.7% conversion of fuel nitrogen to N_2O. This suggests that the downstream introduction of the coal results in the release of more of the char nitrogen into regions where N_2O formation is favored. Thus, the relationship between char nitrogen release and temperature profile is indicated to be important in determining N_2O emissions.

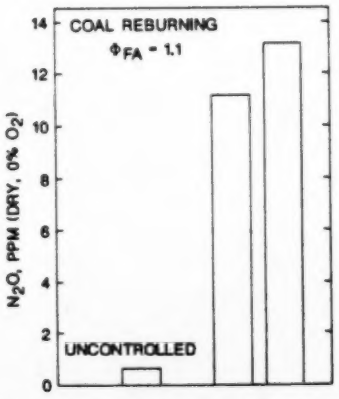

Fig. 6. Production of N_2O by coal reburning. Stoichiometry indicated is that of the fuel-rich reburning zone. Primary is gas fired. The two bars represent a repeat.

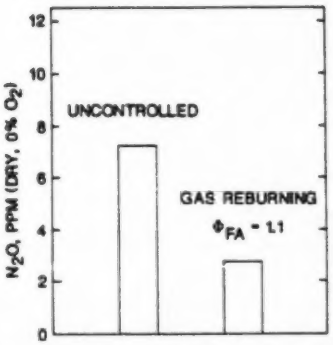

Fig. 7. Reduction of N_2O by natural gas reburning. Stoichiometry indicated is that of the fuel-rich reburning zone. Primary is fired on Utah coal.

Figure 7 shows that natural gas as a reburning fuel exerts an opposite influence to that of coal. The stoichiometries were the same as those of Fig. 6. A coal-fired primary yielded about 7 ppm N_2O under uncontrolled conditions. Application of gas reburning reduced the N_2O emissions to below 3 ppm. The kinetic mechanism shows that N_2O should be effectively destroyed in the fuel-rich zone by reaction with H-atoms (Reaction 11). Roby and Bowman [18] also show direct evidence of the poor survivability of N_2O in fuel-rich regions. Thus, if the char is fully burned out by the gas addition point, then few N_2O precursors will remain at the air staging point. This would account for the low N_2O exhaust concentration.

CONCLUDING REMARKS

The work presented here demonstrates that significant N_2O is formed in postflame environments into which cyano species are introduced. The measurements also show that the introduction of cyano species into flame zones does not result in N_2O emissions. This occurs because the high radical concentrations open competing routes for precursor reaction (e.g., NCO + O), and because of an increase in the rate of N_2O destruction. For the same reason, net formation occurs only within fuel-lean environments where equilibrated H-atom concentrations are low.

For this mechanism to contribute to the N_2O generated in coal flames, a source of cyano species in the postflame region must be postulated. The coal char provides a plausible vehicle for carrying fixed nitrogen beyond the flame zone. The literature suggests that HCN can be formed from char nitrogen in these environments from either direct devolatilization or gasification reactions. Imperfect flame zone mixing may also provide for HCN transport into the cooler regions of large-scale flame where N_2O formation can occur.

The N_2O emissions observed from heavy oil flames may be formed by similar mechanisms. Upon heating, a portion of the oil droplets are reduced to an oil coke solid, into which a portion of the initial fuel nitrogen is bound. The subsequent reaction of the solid could include a gasification step, in which N_2O is formed in a manner analogous to that for coal char. This implies that high nitrogen residual fuels can be expected to produce N_2O, but distillate fuels may not. Alternatively, imperfect flame zone mixing could also transport HCN to cooler portions of the flame where N_2O formation could occur.

Finally, it must be noted that the N_2O emissions for the coal flames reported here are much below the values typically reported in the field literature (although they are well above the corresponding gas flame results). For the present results, this appears to be due to an almost complete burnout of the char-nitrogen before the favorable temperature for N_2O emission is reached. Although N_2O formation in large-scale facilities may be augmented by increase turbulent transport of HCN into cold regions, it must also be remembered that much of the reported field data were obtained using sampling protocols that favored N_2O formation within the sampling containers [14, 15]. This suggests that much of the field data base is artificially high. The mechanism does, however, suggest that N_2O emissions may be elevated from combustion configurations in which the fuel nitrogen is released at temperatures where N_2O formation is favored (e.g., fluidized bed combustors).

We are pleased to acknowledge the contributions of S. L. Chen and T. C. Grogan to the experimental and analytical work. Discussions with R. F. Weiss of Scripps Institute of Oceanography were key to implementing the analytical technique. G. S. Samuelsen and R. K. Lyon are thanked for their comments on the manuscript. This work was supported by the U.S. Environmental Protection Agency–Air and Energy Engineering Research Laboratory—through Contract No. 68-02-4247. This article has been reviewed in accordance with the Agency's peer and policy review, and has been approved for publication. Certain portions of the kinetic mechanism development and verification were supported by the U.S. Department of Energy–Pittsburgh Energy Technology Center—through Contract No. DE-AC22-84PC70771.

REFERENCES

1. Crutzen, P. J., *J. Geophys. Res.* 76:7311 (1971).
2. McElroy, M. B., and McConnell, J. C., *J. Atmos. Sci.* 28:1095 (1971).
3. Crutzen, P. J., and Howard, C. J., *Pure Appl. Geophys.* 116:497 (1978).
4. Donner, L., and Ramanathan, V., *J. Atmos. Sci.* 37:119 (1980).
5. Lacis, A., Hansen J., Lee P., Mitchell, T., and Lebedeff, S., *Geophys. Res. Lett.* 8:1035 (1981).
6. Ramanathan, V., Cicerone, R. J., Singh, H. H., and Kiel, J. T., *J. Geophys. Res.* 90:5547 (1985).
7. Weiss, R. F., *J. Geophys. Res.* 86:7185 (1981).
8. Hao, W. M., Wofsy, S. C., McElroy, M. R., Beer, J. M., and Toqan, M. A., *J. Geophys. Res.* 92:3092 (1987).
9. Pierotti, D., and Rasmussen, R. A., *Geophys. Res. Lett.* 3:265 (1976).

10. Weiss, R. F., and Craig, H., *Geophys. Res. Lett.* 3:751 (1976).
11. Castaldini, C., DeRosier, R., Waterland, L. R., and Mason, H. B., *Proc. of the 1982 Joint Symposium on Stationary Combustion NO_x Control*, EPA-600/9-85-022b (NTIS PB85-235612), 1985, Vol. #, p. 46-1.
12. Kramlich, J. C., Nihart, R. K., Chen, S. L., Pershing, D. W., and Heap, M. P., *Combust. Flame* 48:101 (1982).
13. Muzio, L. J., in *EPA/NOAA/NASA/USDA N_2O Workshop* (J. C. Kramlich, R. K. Lyon, and W. S. Lanier, Eds., EPA-600/8-88-079, U.S. Environmental Protection Agency, 1988, vol. 1, pp. 4–13.
14. Muzio, L. J., and Kramlich, J. C., *Geophys. Res. Lett.* 15:1369 (1988).
15. Lyon, R. K., and Cole, J. A., *Combust. Flame* (in press).
16. Kau, C. J., and Tyson, T. J., *Fundamental Combustion Research Applied to Pollution Formation*, vol. IV—Engineering Analysis, EPA-600/7-87-027, 1987, U.S. Environmental Protection Agency.
17. Glarborg, P., Miller, J. A., and Kee, R. J., *Combust. Flame* 65:177 (1986).
18. Roby, R. J., and Bowman, C. T., *Combust. Flame* 70:119 (1987).
19. Mulcahy, M. F. R., and Smith, I. W., *Rev. Pure Appl. Chem.* 19:81 (1969).
20. Song, H. H., Beer, J. M., and Sarofim, A. F., *Combust. Sci. Technol.* 28:177 (1982).
21. Levy, J. M., Chan, L. K. Sarofim, A. F., and Beer, J. M., *Eighteenth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 1981, p. 111.
22. Kasoaka, S., Sasoloka, E., and Ozaki, A., *Nenryo Kyokai Shi* 62:669 (1983).
23. Zahniser, M. S., and McMurdy, K., and Kolb, C. E., *Chem. Phys. Lett.* (in press).

Received 14 December 1987; revised 27 October 1988

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

This article documents research that was conducted under the auspices of the U.S. Environmental Protection Agency (USEPA). As an arm of the government, the USEPA has a paid up, non-exclusive, irrevocable, worldwide license to reproduce, prepare derivative works, and distribute to the public all of the material contained herein, and to grant others acting on its behalf the right to do so. The USEPA grants to the National Technical Information Service, Department of Commerce, the right to act as its agent in the distribution of this material.